No longer pining for organic molecules to make particles in the air

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Tiny particles in the air called secondary organic aerosols hang around a lot longer than previously thought.

(PhysOrg.com) -- The fresh scent of pine has helped atmospheric scientists find missing sources of organic molecules in the air -- which, it could well turn out, aren't missing after all. In work appearing in this week's *Proceedings of the National Academy of Sciences* Early Edition Online, researchers examined what particles containing compounds such as those given off by pine trees look like and how quickly they evaporate. They found the particles evaporate more than 100 times slower than expected by current air-quality models.

"This work could resolve the discrepancy between field observations and models," said atmospheric chemist Alla Zelenyuk. "The results will affect how we represent organics in climate and air quality models, and could have profound implications for the science and policy governing control of submicron particulate matter levels in the atmosphere."

Zelenyuk and colleagues at the Department of Energy's Pacific Northwest National Laboratory were able to measure evaporation from atmospheric particles in a much more realistic manner than ever before. This allowed them to show that they are not liquids, as has been assumed for two decades, and to get an accurate read on how fast these particles evaporate. What researchers previously thought takes seconds actually takes days.

Airy Organics

Secondary organic aerosols are tiny bits of chemically modified organic compounds floating in the air. They absorb, scatter or reflect sunlight, and serve as cloud nuclei, making them an important component of the atmosphere.

For a couple of decades, researchers have interpreted laboratory and field measurements under the assumption that these particles are liquid droplets that evaporate fast, which is central to the way these particles are modeled. However, to this day researchers have failed to explain the high amounts observed in the real atmosphere. The never-ending search for extra sources of organics has been frustrating for scientists studying these aerosols.

To re-examine the assumption, researchers at PNNL used equipment that could study the particles under realistic conditions. Zelenyuk developed a sensitive and high-precision instrument called SPLAT II that can count, size and measure the evaporation characteristics of these particles at room temperature. Research and development for SPLAT II occurred partly in EMSL, DOE's Environmental Molecular Sciences Laboratory at PNNL.

SPLAT Surprises

First, the researchers created secondary organic aerosol particles in the lab by oxidizing alpha-pinene, the molecule that makes pine trees smell like pine. Oxidation is the same thing that happens to iron when it rusts, and happens a lot in the atmosphere when aerosols come into contact with gases such as ozone, which is a pollutant when it is low in the atmosphere.

For comparison, the researchers also made particles from other, well-understood organic molecules that are known to form solids or liquid droplets, such as one called DOP. Lastly, they allowed these other organic molecules and the pine-scented SOA particles to mingle to simulate what likely happens in the outdoors.

Monitoring the various particles with SPLAT II for up to 24 hours, the research team found that DOP particles behaved as expected. Organics evaporated from the particles quickly, and faster if the particle was smaller, which is how liquid particles evaporate.

But the pinene-based particles did not. About 50 percent of their volume evaporated away within the first 100 minutes. Then they clammed up, and only another 25 percent of their volume dissipated in the next 23 hours. In addition, this fast-slow evaporation occurred similarly whether the particle was big or small, indicating the particles were not behaving like a liquid.

This lack of evaporation could account for the inability of scientists to find other sources of atmospheric organics. "Our findings indicate that there may, in fact, be no missing SOA," said Zelenyuk.

Slowing Spectators

In the world, the SOAs from pinene co-exist with other organic molecules, and some of these slam onto the particle and coat it. Experiments with the co-mingled SOAs and organic compounds showed the researchers that coated particles evaporate even slower than single-source SOA.

Zelenyuk then tested how close to reality their lab-based SOAs were. Using air samples gathered in Sacramento, Calif., the team found the behavior of atmospheric SOAs (whether from trees and shrubs or pollution) paralleled that of the co-mingled pinene-derived SOAs in the lab and did not behave like liquids.

The results suggest that in the real atmosphere, SOA evaporation is so slow that scientists do not need to include the evaporation in certain models. The researchers hope that incorporating this information into atmospheric models will improve the understanding of aerosols' role in the climate.

More information: More on SPLAT II: www.emsl.pnl.gov/news/viewArti … le.jsp?articleId=106

Timothy D. Vaden, Dan Imre, Josef Beránek, Manish Shrivastava, and Alla Zelenyuk, On the Evaporation Kinetics and Phase of Laboratory and Ambient Secondary Organic Aerosol, *Proc Natl Acad Sci USA, Early Edition* online the week of January 24, DOI:10.1073/pnas.1013391108

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